



Short communication

## Engineering aspects of the hybrid supercapacitor with H-insertion electrode

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### HIGHLIGHTS

- It is critical to balance two electrode in H-insertion hybrid supercapacitor.
- H<sub>2</sub> formed from charging process can be self-oxidized preventing pressure buildup.
- O<sub>2</sub> evolution on the double-layer carbon electrode can be avoided during charging.

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### ABSTRACT

A hybrid supercapacitor, which was assembled with an H-insertion negative carbon electrode and an electrochemical double-layer positive electrode, was studied and its structure was optimized. The electrochemical performance of the individual electrode with different negative to positive electrode mass ratios was investigated. It has been demonstrated that the performance of the hybrid supercapacitor is closely related to the electrode balance. The results indicated that for carbon electrodes used in the study, the capacity of the H-insertion electrode could be fully utilized when the mass ratio of the negative to positive electrode is about 1:6.

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### 1. Introduction

The demand for efficient, long-lived and environmentally-friendly energy storage systems has significantly increased in recent years. Among those advanced energy devices, the secondary battery and supercapacitor have been found to meet social requirements in many areas. Secondary batteries are well-known with to have high energy density but relative low power density and short cycle life. Comparatively, even with low energy density, a supercapacitor can still play an important role in applications which require high power on-demand, fast charging and long cycle life. Since both systems cannot fulfill the needs for high energy density and high power density, a hybrid system which combines a battery electrode with an electrochemical capacitive electrode was suggested [1–13]. Differing from the traditional electrochemical capacitor with non-faradic double-layer charge storage,

the hybrid device combines a faradic type rechargeable battery electrode e.g. NiOOH, MnO<sub>2</sub>, Li insertion carbon etc. with a double-layer carbon electrode. Such design would demonstrate higher energy density than a traditional double-layer capacitor, and higher power density than a rechargeable battery. However, faster capacity degradation and thus limitation of recyclability would be the trade-off for a hybrid system, in order to gain more energy density. This is due to the fact that all active battery materials suffer from irreversible reactions including reaction with electrolyte, structure change, formation of SEI layers on the Li insertion carbon electrode during cycling, etc. To alleviate those problems, a novel hybrid supercapacitor with H-insertion electrode was reported recently [9]. In this hybrid configuration, an electrochemical double-layer electrode is coupled with a hydrogen insertion electrode. During the charge process, a water molecule accepts an electron from the electrode, the generated H atom becomes adsorbed onto the electrode surface and subsequently inserts into the host electrode. The H atoms in the carbon host become oxidized during the discharge. It is worth emphasizing that H is from the electrochemical reduction of H<sub>2</sub>O. Hydrogen atoms are formed at

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the surface of the electrode when  $\text{H}_2\text{O}$  molecules gain electrons from carbon electrode.  $\text{C}(\text{e}) + \text{H}_2\text{O} \rightleftharpoons \text{CH}_{\text{ads}} + \text{OH}^-$ . Thus, the kinetics of hydrogen atoms electro-generation will not be related to the concentration of  $\text{H}^+$  in the electrolyte, but to the electrode surface catalytic conditions. The advantage for the system is its excellent cycleability because unlike other hybrid chemistries, the carbon electrode itself is just an inert host for the inserted H; there is no solid electrolyte interface (SEI) layer and the supply of H is almost infinite [9]. It is always critical to balance the negative and positive electrode in an electrochemical device. Due to the uniqueness of the H-insertion hybrid capacitor, such asymmetric design becomes crucial. Since both surface and bulk processes are involved at the negative H-insertion electrode, and only interfacial surface processes occur on the positive double-layer electrode, the electrode balance has to be optimized to deliver maximum energy and power. In addition, such asymmetric configuration should also accommodate the unique over-charge self-prevention mechanism [9]. The efforts to optimize the electrode balance are reported.

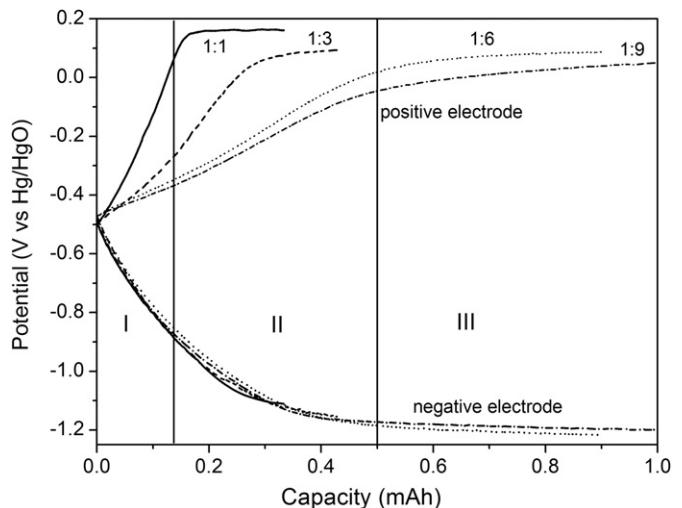
## 2. Experimental details

Commercial activated carbon (AC) with a surface area of  $1114 \text{ m}^2 \text{ g}^{-1}$  and average pore-size of  $3.26 \text{ nm}$  was purchased from Sinopharm Chemical Reagent Co., Ltd. The activated carbon was reflux-washed with acetone in a Soxhlet extractor for about 24 h to remove most of the physical bonded surface functional groups. Then the pre-treated activated carbon powder (90 wt.%) was mixed with Teflon suspension (10 wt.% of dry material). After thoroughly mixing, the paste was left for air dry. The resulting Teflon bonded carbon was rolled into a thin film with geometric surface area of  $1 \text{ cm}^2$ , thickness of  $0.5 \text{ mm}$  and sandwiched into two pieces of nickel foam current collector. The same carbon material was used in the both electrodes. The mass ratios of the activated carbon inside the negative and positive electrodes were 1:1, 1:3, 1:6, 1:9 in this study. The total mass of negative electrode was 10 mg. Two electrodes then mounted into a home-made Teflon holder face to face with a non-woven separator in between.

Aqueous potassium hydroxide solution (30 wt.%) was used as an electrolyte in all measurements. A CH Instruments 660C electrochemical workstation was used for electrochemical measurements. A National Instruments USB-6212 data acquisition card controlled by Labview software was used to monitor the potential change for the individual negative and positive electrodes against a  $\text{Hg}/\text{HgO}$  reference electrode during the charge/discharge process. A Micromeritics ASAP 2020 porosimeter was used for the surface area and porosity measurements. Nitrogen was used as absorbent gas. Density function theory (DFT) software from Micromeritics was also used.

## 3. Result and discussion

Fig. 1 shows the potential profiles for the positive and negative electrodes with various mass ratios during the charge processes. When both electrodes have the same weight (10 mg), the slopes of the potential curves (solid line) for the both positive and negative electrodes were almost symmetrical, indicating a typical symmetric double-layer capacitor. When the mass ratio of the negative to positive electrodes increased to 1.3, 1:6 and 1:9, respectively, while the mass of positive electrode remained the same (10 mg), the slopes for the charge curves became flatter as the mass of the positive electrode increased. The capacitances of the positive electrodes with the weight of 10, 30, 60 and 90 mg were found to be 0.98, 1.6, 3.4 and 4.1 F, respectively. It is interesting to note that even though the double-layer capacitance increased as the weight of electrode increased, the capacitance increase is not proportional to the weight increase. It may result from the impact

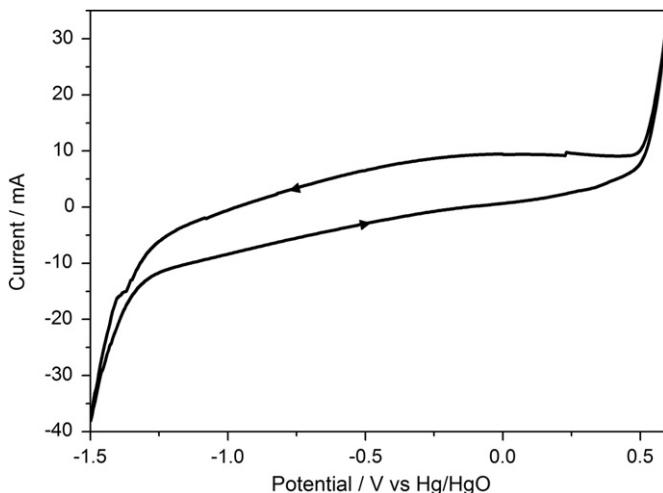


**Fig. 1.** The charging curves for the positive and negative electrodes with charging current density of  $2 \text{ mA cm}^{-2}$  against  $\text{Hg}/\text{HgO}$  reference electrode. The solid, dashed, dotted and dash-dotted lines represented charging curves of negative and positive electrodes with mass ratios: 1:1, 1:3, 1:6 and 1:9, respectively.

of electrode thickness on efficiency. Apparently the heavier the electrode, thus the thicker the electrode, the less efficient it was. Such loss of efficiency is believed to be caused by the poor diffusion and distribution of ions in the matrix of the porous electrode. This phenomenon illustrates the importance of the electrode optimization and engineering. At the same time, the potential curves of negative electrodes were almost identical since they carried the same weight of active materials in all the cases.

Three distinguishable regions can be observed in the charging curves. In the beginning of the charge, charges were used to build up the double-layer for the both electrodes (region I). In this region, the electrochemical double-layer capacitance on the positive electrode increased with the increase of electrode weight. When the charges continuously passed into electrodes, the double-layer of the negative electrode was fully charged when the potential of the negative electrode reached about  $-0.9 \text{ V}$ . The atomic hydrogen began to generate and hydrogen under-potential deposition took place (region II). In this region, on the negative electrode, the generated hydrogen atoms first became adsorbed on the surface of the carbon electrode and then the majority of them were inserted into the carbon nanostructure due to the low surface coverage of H [14]. Inevitably, a small amount of the adsorbed hydrogen atoms would recombine with each other and form hydrogen molecules. Once the charging of the negative electrode entered region III where the electrode potential reached  $-1.2 \text{ V}$  vs.  $\text{Hg}/\text{HgO}$ , the potential curves started to flatten out. This indicated that as the surface coverage of hydrogen increased, most of electro-sorbed H recombined to form  $\text{H}_2$  [14]. Fig. 2 provides further prove for the assumption. Fig. 2 shows the cyclic voltammogram for the carbon electrode. Clearly, massive hydrogen generation starts at about  $-1.2 \text{ V}$  vs.  $\text{Hg}/\text{HgO}$ .

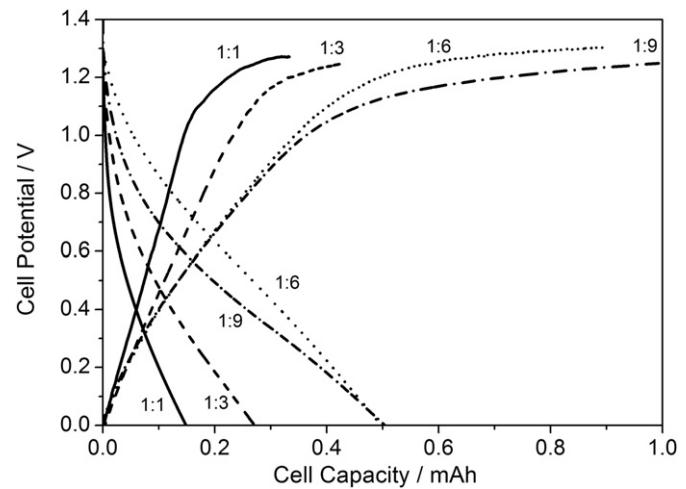
On the positive electrode, the electrochemical processes are related to those on the negative electrode. In the region I, the charging current was used to charge the double-layer for all the positive electrodes with different mass. In region II, the double-layer was fully charged for the 10 mg electrode, the  $\text{O}_2$  started to evaluate at potential  $0.2 \text{ V}$  vs.  $\text{Hg}/\text{HgO}$ , which correlated well with the oxygen evolution potential in Fig. 2. However, the double-layers for the positive electrodes with increased mass were not fully charged in region I. Therefore, while in region II H-insertion took place on the negative electrode, the positive charges were still used



**Fig. 2.** Cyclic voltammogram of the activated carbon electrode recorded in a three electrode cell at  $20 \text{ mV s}^{-1}$  with 30% KOH aqueous solution as electrolyte. Hg/HgO was used as reference electrode; Ni-mesh as counter electrode.

for constructing the double-layer until the potential reached the  $\text{H}_2$  oxidation potential (about 0.05 V vs. Hg/HgO); at which point the  $\text{H}_2$  generated from the negative electrode became oxidized. It is evident that the larger the electrode mass, the longer the positive charges are used to charge the double-layer. It is worthwhile to emphasize that optimizing the electrode balance is not only critical for achieving high energy and power for the capacitor, but also important for the safety of the device. Obviously, in an asymmetric configuration  $\text{O}_2$  evolution will never happen during the charging, since the positive electrode potential will be maximized at  $\text{H}_2$  oxidation potential. The observation of the hydrogen self-oxidation during the charging process illustrated one of the advantages for the current hybrid supercapacitor. Since the insertion of adsorbed H atom into the carbon interlayer space competes with the hydrogen electrochemical or chemical recombination processes, the molecular form of hydrogen will inevitably be generated during the H-insertion process. Accumulation of  $\text{H}_2$  would cause the capacitor internal pressure increase. But in present hybrid configuration, the hydrogen molecules produced at the negative electrode during the charging process diffuse through the separator and eventually be consumed at the positive electrode. This would ensure the safety of the supercapacitor under overcharging conditions, even though this may decrease its efficiency. It should be emphasized that the larger the positive electrode mass is, more gaseous  $\text{H}_2$  is allowed to be accumulated in the sealed supercapacitor capacitor. Such gas accumulation will result in the increase of internal pressure, thus the risk of rupture; and charging energy will be wasted for generating  $\text{H}_2$ , thus resulting of low “round-trip efficiency” for the capacitor. Of course, if the mass of positive electrode is not maximized, the energy density will be compromised. It is interesting to notice that the charge curve of positive electrode with the weight of 90 mg did not fully flatten out: the potential still slowly raised up as the charging went on. This phenomenon indicates that, in this electrode, charges were not totally used for the oxidation of hydrogen: the double-layer was continuously built-up.

Fig. 2 shows the cyclic voltammogram for the carbon electrode in 30 wt.% potassium hydroxide aqueous solution recorded in the potential range of  $-1.5 \text{ V}$  and  $0.5 \text{ V}$ . It is clearly shown that there is no visible anodic current above the current used to construct the double-layer in the potential range of  $0.05\text{--}0.1 \text{ V}$ . A significant anodic and cathodic current were observed around  $0.2 \text{ V}$  and  $-1.2 \text{ V}$ , respectively, which can be assigned to the  $\text{O}_2$  and  $\text{H}_2$  generation. The results in Fig. 2 are consistent with those in Fig. 1.



**Fig. 3.** Charge-discharge curves of the hydrogen-insertion hybrid super-capacitor under current density of  $2 \text{ mA cm}^{-2}$  with different mass ratios of activated carbon inside negative and positive electrodes. The solid, dash, dot and dash dot lines represented negative to positive electrode mass ratios of 1:1, 1:3, 1:6 and 1:9, respectively.

Fig. 3 shows the charge-discharge curves of the H-insertion hybrid super-capacitors made with various mass ratios of the negative and positive electrodes. It shows that the capacity of the hybrid supercapacitor was found to increase until the mass ratio reached about 1:6. The further increase of the mass ratio did not affect the capacity of the supercapacitor, because the limiting capacity of the H-insertion electrode was reached. The double-layer capacitance of the positive electrode and overall capacity of the supercapacitor at various mass ratios are tabulated in Table 1. It clearly demonstrated that with the proper adjustment of the electrode balance, the capacitance of the hybrid capacitor can be substantially increased. Obviously, the hydrogen evolution in the negative electrode will significantly affect the efficiency, therefore the hydrogen generation over-potential should be increased by modifying the electrode surface catalytic properties and the electrode balance should be optimized to compromise both the capacity and efficiency. For example, a 1:6 mass ratio of the negative and positive electrode was shown to be the optimized ratio for the carbon studied in this paper. In the current study, the same kind of active carbon was used for both electrodes. To further improve the performance of the hybrid H-insertion super-capacitor, the selection of proper materials for each electrode should also be considered. The materials which can be used in the negative electrode include carbon materials with large intra-layer distance, which can efficiently increase the amount of hydrogen storage, or those materials with adsorbed catalyst poisons, which can enhance the electrochemical hydrogen insertion, prevent the surface adsorbed H from recombination, and thus delay the hydrogen evolution on the negative electrode [14,15]. The materials selected for the positive electrode include carbon materials with high

**Table 1**

Comparison of the capacity of double-layer contribution and overall capacity with the different weight ratios of negative and positive electrode in the hybrid supercapacitor.

Weight ratio	Double-layer capacitance of positive electrode (F)	Capacity of negative electrode (mAh)	Overall capacity of devices (mAh)	Capacity limitation electrode
1:1	0.98	0.14	0.14	Positive (double-layer)
1:3	1.6	0.27	0.27	Positive (double-layer)
1:6	3.4	0.56	0.51	Negative (H-insertion)
1:9	4.1	0.68	0.51	Negative (H-insertion)

surface area, especially those hierarchically ordered meso/micro porous carbon materials with suitable porous structure [16–19]. The investigation of the various carbon materials in the H-insertion hybrid supercapacitor is in progress in our labs.

#### 4. Conclusion

Hybrid H-insertion supercapacitors combining an electrochemical double-layer capacitor positive electrode with a H-insertion negative electrode of various mass ratios were studied. During the charging process, the negative electrode went through double-layer construction, hydrogen UPD/insertion, and hydrogen insertion/evolution stages. Meanwhile, the positive electrode also experienced double-layer charging and hydrogen oxidation. The observed hydrogen oxidation on the positive electrode would ensure the safety of the hybrid supercapacitor during overcharging conditions, since the H<sub>2</sub> generated on the negative electrode becomes oxidized on the positive electrode. The optimized configuration of the asymmetric supercapacitor is critical for the capacity, safety and “round-trip efficiency”. In our study, the optimized mass ratio of the negative to positive electrode was found to be 1:6.

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